

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 283/02, C08L 67/04, 51/08		A1	(11) International Publication Number: WO 99/06456
			(43) International Publication Date: 11 February 1999 (11.02.99)
(21) International Application Number: PCT/US98/15968			(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 31 July 1998 (31.07.98)			
(30) Priority Data:			
08/903,864 31 July 1997 (31.07.97) US			
08/903,862 31 July 1997 (31.07.97) US			
08/903,866 31 July 1997 (31.07.97) US			
(71) Applicant: KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).			Published <i>With international search report.</i>
(72) Inventors: WANG, James, H.; 1325 E. Overland Road, Appleton, WI 54915 (US). SOERENS, Dave, A.; 736 Kensington Road, Neenah, WI 54956 (US). SCHERTZ, David, M.; 1107 Noble Creek Drive, Atlanta, GA 30327 (US). RHIM, Hannong; 2648 Long Lake Drive, Roswell, GA 30075 (US).			
(74) Agents: KYRIAKOU, Christos, S.; Jones & Askew, LLP, 37th floor, 191 Peachtree Street, N.E., Atlanta, GA 30303 (US) et al.			
(54) Title: MODIFIED POLYLACTIDE COMPOSITIONS, WATER-RESPONSIVE, BIODEGRADABLE FILMS AND FIBERS COMPRISING POLYLACTIDE AND POLY(VINYL ALCOHOL) AND METHODS FOR MAKING THE SAME			
(57) Abstract			
<p>The present invention discloses water-responsive films and fibers. More particularly, the present invention includes films and fibers comprising blends of a polyvinyl alcohol and a polylactide and methods of making such films and fibers. In a preferred embodiment, the invention includes films and fibers comprising a blend of polyvinyl alcohol and modified polylactide and a method of modifying a polylactide. In a preferred embodiment, the present invention includes a hydrolytically modified, biodegradable polymer and a method of hydrolytically modifying a biodegradable polymer. In a preferred embodiment, the invention is a method of grafting polar groups onto polylactides and modified polylactide compositions produced by the method. The modified compositions, blends, films and fibers are useful as components in flushable and degradable articles.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5 **MODIFIED POLYLACTIDE COMPOSITIONS, WATER-RESPONSIVE,
 BIODEGRADABLE FILMS AND FIBERS COMPRISING
 POLYLACTIDE AND POLY(VINYL ALCOHOL)
 AND METHODS FOR MAKING THE SAME**

10

FIELD OF THE INVENTION

 The present invention relates to hydrolytically modified, biodegradable polymers and methods of hydrolytically modifying biodegradable polymers. More particularly, the present invention relates to modified polylactide compositions and
15 methods of modifying polylactides. In a preferred embodiment, the invention relates to a method of grafting polar groups onto polylactides, grafted polylactide compositions, and films and fibers comprising the same. The present invention also relates to water-responsive, biodegradable films and fibers comprising a polylactide and a poly(vinyl alcohol) and a method of varying the water-responsiveness of such films and fibers.

20

BACKGROUND OF THE INVENTION

 Even though the amount of plastics used in a variety of consumer goods, packaging and medical articles has not significantly increased over the past twenty years, the common perception is that more and more non-degradable plastics are filling up our
25 limited landfill space. Despite this perceived disadvantage, plastics continue to be used in the manufacture of consumer goods, packaging and medical articles because plastics offer many advantages over the more traditional materials: wood, glass, paper, and metal. The advantages of using plastics, more precisely polymers, include decreased manufacturing time and costs, improved mechanical and chemical properties, and decreased weight and
30 transportation costs. It is the improved chemical resistance properties of the majority of plastics that result in their non-degradability.

 Disposal of waste materials, including food waste, packaging materials and medical waste, into a typical landfill provides a relatively stable environment in which none of these materials is seen to decompose at an appreciable rate. Alternative waste
35 disposal options have been increasingly discussed and utilized to divert some fraction of waste from entombment. Examples of these alternative disposal options include

municipal solid waste composting, anaerobic digestion, enzymatic digestion, and waste water sewage treatment.

5 Much controversy is associated with the disposal of medical waste. Both government agencies and members of the private sector have been increasingly directing in-depth scrutiny and funds toward this subject. Admittedly, concerns over the fate of materials contaminated with infectious substances are valid and proper measures to insure the safety of health care workers and the general public should be taken.

10 Currently, medical waste can be categorized as either reusable or disposable. Categorization as to whether certain waste is reusable or disposable is customarily determined according to the material from which the article was constructed and the purpose for which the article was used.

15 After use, reusable medical articles are cleansed and sterilized under stringent conditions to ensure disinfection. In comparison, disposable medical articles are usually only used once. Even then, disposing procedures are not straightforward, rather they often involve several steps to safeguard against potential hazards. Typically, after use, disposable medical articles must be disinfected or sterilized, adding a significant cost prior to disposal into a specially designated landfill or waste incinerator. As a result, the disposal cost for the contaminated single use articles is quite high.

20 Despite the high cost of disposal, single use medical articles are desirable because of the assurance of clean and uncontaminated equipment. Many times in the medical context, sterilization procedures conducted improperly can result in detrimental effects such as the transmission of infectious agents from one patient to another. Improper sterilization can also be disastrous in a laboratory setting, where, for example, contaminated equipment can ruin experiments resulting in tremendous costs of time and money.

25 Currently, disposable medical fabrics are generally composed of thermoplastic fibers such as polyethylene, polypropylene, polyesters, polyamides and acrylics. These fabrics can also include mixtures of thermoset fibers such as polyamides, polyarimides and cellulose. The fabrics are typically 10 to 100 grams per square yard in weight and can be woven, knitted or otherwise formed by methods well known to those in the textile arts while the non-woven fabrics can be thermobonded, hydroentangled, wet laid or needle punched. Films can be formed by blow or cast extrusion or by solution casting. Once used, these fabrics and films are difficult and costly to dispose of and are non-degradable.

35 The use of polymers for various disposable articles is widespread and well known in the art. In fact, the heaviest use of polymers in the form of film and fibers occurs in the packaging and the disposable article industries. Films employed in the

packaging industry include those used in food and non-food packaging, merchandise bags and trash bags. In the disposable article industry, the general uses of polymers occurs in the construction of diapers, personal hygiene articles, surgical drapes and hospital gowns, instrument pads, bandages, and protective covers for various articles.

5 In light of depleting landfill space and inadequate disposal sites, there is a need for polymers which are water-responsive. Currently, although polymers such as polyethylene, polypropylene, polyethylene terephthalate, nylon, polystyrene, polyvinyl chloride and polyvinylidene chloride are popular for their superior extrusion and film and fiber making properties, these polymers are not water-responsive. Furthermore, these
10 polymers are generally non-compostable, which is undesirable from an environmental perspective.

 Polymers and polymer blends have been developed which are generally considered to be water-responsive. These are polymers which purportedly have adequate properties to permit them to breakdown when exposed to conditions which lead to
15 composting. Examples of such arguably water-responsive polymers include those made from starch biopolymers and polyvinyl alcohol.

 Although materials made from these polymers have been employed in film and fiber containing articles, many problems have been encountered with their use. Often, the polymers and articles made from these polymers are not completely water-responsive or
20 compostable. Furthermore, some water-responsive polymers may also be unduly sensitive to water, either limiting the use of the polymer or requiring some type of surface treatment to the polymer, often rendering the polymer non water-responsive. Other polymers are undesirable because they have inadequate heat resistance for wide spread use.

25 Personal care products, such as diapers, sanitary napkins, adult incontinence garments, and the like are generally constructed from a number of different components and materials. Such articles usually have some component, usually the backing layer, constructed of a liquid repellent or water-barrier polymer material. The water-barrier material commonly used includes polymer materials such as films of polyethylene or
30 copolymers of ethylene and other polar and nonpolar monomers. The purpose of the water-barrier layer is to minimize or prevent absorbed liquid that may, during use, exude from the absorbent component and soil the user or adjacent clothing. The water-barrier layer also has the advantage of allowing greater utilization of the absorbent capacity of the product.

35 Although such products are relatively inexpensive, sanitary and easy to use, disposal of a soiled product is not without its problems. Typically, the soiled products are disposed in a solid waste receptacle. This adds to solid waste disposal accumulation

and costs and presents health risks to persons who may come in contact with the soiled product. An ideal disposal alternative would be to use municipal sewage treatment and private residential septic systems by flushing the soiled product in a toilet. Products suited for disposal in sewage systems are termed "flushable." While flushing such articles would be convenient, prior art materials do not disintegrate in water. This tends to clog toilets and sewer pipes, frequently necessitating a visit from a plumber. At the municipal sewage treatment plant, the liquid repellent material may disrupt operations by plugging screens and causing sewage disposal problems. It therefore is necessary, although undesirable, to separate the barrier film material from the absorbent article prior to flushing.

In addition to the article itself, typically the packaging in which the disposable article is distributed is also made from a water-barrier, specifically water-resistant, material. Water-resistivity is necessary to prevent the degradation of the packaging from environmental conditions and to protect the disposable articles therein. Although this packaging may be safely stored with other refuse for commercial disposal, and especially in the case of individual packaging of the products, it would be more convenient to dispose of the packaging in the toilet with the discarded, disposable article. However, where such packaging is composed of a water-resistant material, the aforementioned problems persist.

The use of lactic acid and lactide to manufacture a water-stable polymer is known in the medical industry. Such polymers have been used in the past for making water-stable sutures, clamps, bone plates and biologically-active, controlled-release devices. Processes developed for the manufacture of such polymers utilized in the medical industry have incorporated techniques which respond to the need for high purity and biocompatibility in the final product. These processes, however, are typically designed to produce small volumes of high dollar-value products, with less emphasis on manufacturing cost and yield.

It is generally known that lactide polymers or poly(lactides) are unstable. However, the consequence of this instability has several aspects. One aspect is the biodegradation or other forms of degradation which occur when lactide polymers, or articles manufactured from lactide polymers, are discarded or composted after completing their useful life. Another aspect of such instability is the degradation of lactide polymers during processing at elevated temperatures as, for example, during melt-processing by end-user purchasers of polymer resins.

In the medical area, there is a predominant need for polymers which are highly stable and therefore desirable for use in medical devices. Such a demand has historically

been prevalent in the high value, low volume medical specialty market, but is now also equally prevalent in the low value, high volume medical market.

As described in U.S. Patent No. 5,472,518, compositions comprised of multilayer polymer films are known in the art. The utility of such structures lies in the manipulation of physical properties in order to increase the stability or lifetime during use of such structure. For example, U.S. Patent No. 4,826,493 describes the use of a thin layer of hydroxybutyrate polymer as a component of a multilayer structure for use as a barrier film in diapers and ostomy bags.

Another example of use of multilayer films is found in U.S. Patent No. 4,620,999 which describes the use of a water soluble film coated with, or laminated to, a water insoluble film as a disposable bag. The patent describes a package for body waste which is stable to human waste during use, but which can be made to degrade in the toilet, at a rate suitable for entry into a sewage system without blockage, by adding a caustic substance to achieve a pH level of at least 12. Such structures usually consist of a polyvinyl alcohol film layer coated with polyhydroxybutyrate.

A similar excretion-treating bag which allows for discarding in flush toilet or sludge vessel is described in JP 61-42127. The described bag is composed of an inner layer of water-resistant, water-dispersible resin, such as polylactide, and an outer layer of polyvinyl alcohol. As described in this patent, there are many examples of multilayer films that are utilized in disposable objects. Most of these examples consist of films or fibers which are comprised of external layers of an environmentally degradable polymer and an internal layer of water-responsive polymer. Typically, the external layers are comprised of polycaprolactone or ethylene vinyl acetate and the internal layer is comprised of polyvinyl alcohol. These examples, however, are all limited to compositions consisting of multilayers of different polymers, and do not encompass actual blends of different polymers.

A family of patents, EP 241178, JP 62-223112 and U.S. Patent No. 4,933,182, describes a controlled release composition for treating periodontal disease. The controlled release compositions are comprised of a therapeutically effective agent in a carrier consisting of particles of a polymer of limited water solubility dispersed in a water soluble polymer. Although the carrier of these inventions includes the use of more than one polymer, the disclosed carrier is not a blend because the water soluble polymer of limited solubility is incorporated in the water soluble polymer as particles ranging in average particle size from 1 to 500 microns.

The use of polymers for use in water-responsive articles is disclosed in U.S. Patent No. 5,508,101, U.S. Patent No. 5,567,510, and U.S. Patent No. 5,472,518. This group of patents describes a series of water-responsive compositions comprising a

hydrolytically degradable polymer and a water soluble polymer. The compositions of this group, however, consist of articles constructed from polymers which are first formed into fibers or films and then combined. As such, the compositions are actually mini-layers of the individual polymer films or fibers. Therefore, although the fibers and films of the polymers of such compositions are considered to be in very close proximity with one another, they are not actual blends. The dispersion of one polymer within another in these compositions, is not viewed as approximately uniform since the individual polymers are essentially distinct and separate fibers or films.

U.S. Patent No. 5,525,671 to Ebato et al. describes a method of making a linear lactide copolymer from a lactide monomer and a hydroxyl group-containing monomer. The polymer described by Ebato is a linear lactide copolymer produced by reacting two monomers to form a linear polymer with a block or random structure. Ebato does not disclose graft copolymers.

Polymer blend compositions for making fibers and films that are optimally combined are desirable because they are highly stable. Optimal combination of polymers means that the polymers are connected as closely as possible without the requirement of co-polymerization. Although blended polymer compositions are known, improved polymer blends wherein the fibers and films are more intimately connected are desirable since the resulting composition is then more stable, pliable and versatile.

In addition to the need for polymer compositions that are highly stable, and therefore, suitable for regular use in most disposable articles, there is a simultaneous need for such polymer compositions to be water-responsive. What is needed, therefore, is a water-responsive material that may be utilized for the manufacture of disposable articles. Such a material should be versatile and inexpensive to produce and process. The material should be stable enough for intended use, but degrade under predetermined conditions.

Moreover, there is an increased emphasis on environmentally safe materials and coatings. These environmentally safe coatings reduce the use of solvent-based coatings and rely, to an ever increasing degree, on polar coatings, such as water-based materials. The utility of the graft copolymers of this invention includes, but would not be limited to, materials having a greater affinity for a polar coating.

Therefore, it is an object of this invention to make a hydrolytically modified, biodegradable polymer, and films and fibers containing the same.

Another object of this invention is to make thermally processable polymers, blends, films, fibers and articles.

Another object of this invention is to make commercially viable polymers, films and fibers.

Another object of this invention is to make thermally processable, biodegradable polymers, blends, films and fibers, which are more compatible with polar polymers and other polar substrates.

5 Another object of this invention is to make a hydrolytically modified, biodegradable polymer useful for making flushable, biodegradable polymer compositions and blends, films, fibers and articles containing the same.

Another object of this invention is to make a hydrolytically modified, biodegradable polymer useful for making blends, films and fibers with improved mechanical and physical properties.

10 Another object of this invention is to make a modified polylactide, which has improved compatibility in blends with polar polymers.

Another object of the invention is to make improved blends comprising polylactides.

15 Another object of the invention is to make thermally processable, biodegradable polymer blends, films and fibers, which are more compatible with polar polymers and other polar substrates.

Another object of this invention is to make water-responsive, biodegradable polymers, blends, films, fibers and articles.

20 Another object of this invention is to make water-responsive, biodegradable polymers, blends, films and fibers with improved mechanical and physical properties.

Another object is to develop a method of making water-responsive blends, films fibers and articles, which may be tailored to be water-dispersible, water-weakenable or water-stable.

25 SUMMARY OF THE INVENTION

The present invention discloses water-responsive and biodegradable blends, films and fibers containing polyvinyl alcohol and polylactide. The water-responsive blends, and the films and fibers made therefrom have a wide range of responsiveness, ranging from water-dispersible, to water-degradable, and to water-stable. The present
30 invention also discloses a method of controlling the water-responsiveness of the blends, films and fibers by varying the amount of polyvinyl alcohol from about 1 to about 99 weight percent of the blend and varying the amount of polylactide from about 1 to about 99 weight percent of the blend. The composition ranges responsible for each type of water-responsiveness are disclosed.

35 In a preferred embodiment, the invention includes modified polylactide compositions comprising a polylactide grafted with polar monomers. The present invention describes compositions of polylactide grafted with 2-hydroxyethyl methacrylate

or poly(ethylene glycol) methacrylate, as well as, a reactive extrusion process for making modified polylactide compositions.

5 Polylactides are biodegradable polymers which are commercially viable and thermally processable. By grafting polar monomers onto a polylactide, the resulting modified polylactide is more compatible with polar polymers and other polar substrates. For flushable material development, the modified polylactide compositions of the present invention have enhanced compatibility with water-soluble polymers, such as polyvinyl alcohol and polyethylene oxide, compared to unmodified polylactide. The compatibility of modified polylactide compositions with a polar material can be controlled by the selection of the monomer and the level of grafting. Tailoring the compatibility of blends with modified polylactide compositions leads to better processability and improved physical properties of the resulting blend.

10 The water-responsive compositions disclosed in the present invention have the unique advantage of being biodegradable so that the compositions, and films, fibers and articles made from the compositions, can be degraded in aeration tanks by aerobic degradation and anaerobic digestors by anaerobic degradation in waste water treatment plants. Therefore, articles made from the compositions of the present invention will not significantly increase the volume of sludge accumulated at waste water treatment plants.

20 The fibers of the present invention are useful as components of flushable personal care products, such as liners for diapers, spunbonded nonwovens for clothlike outer covers, etc. The films of the present invention are useful as components of flushable personal care products, such as baffle films for feminine and adult care products, outer covers for diapers, etc.

25 BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a plot of the viscosity versus the shear rate of a grafted polylactide in accordance with the present invention and an ungrafted polylactide, demonstrating the decrease in viscosity of a grafted polylactide versus an ungrafted polylactide.

30 DETAILED DESCRIPTION OF THE INVENTION

Polylactide (PLA) resins are produced by different synthetic methods, such as ring-opening polymerization of lactide or direct condensation polymerization from lactic acid. Both methods of polymerization are useful for the present invention. PLA is a biodegradable polymer having the chemical structure:



The PLA compositions described in the following Examples are made by using a reagent grade PLA purchased from Aldrich Chemical Company of Milwaukee, Wisconsin (Aldrich Catalog number 42,232-6). The PLA purchased from Aldrich Chemical Company is biodegradable and has a number-average molecular weight of approximately 60,000 grams per mol and a weight-average molecular weight of approximately 144,000 grams per mol. This PLA is made up primarily of the L-isomer and has a glass transition temperature (T_g) of 60°C. Any PLA can be selected for use in the present invention, and the molecular weights of the PLA may vary depending on the desired properties and use.

Ethylenically unsaturated monomers containing a polar functional group, such as hydroxyl, carboxyl, amino, carbonyl, halo, thiol, sulfonic, sulfonate, etc., are appropriate for the present invention. Preferred ethylenically unsaturated monomers containing a polar functional group include 2-hydroxyethyl methacrylate (referred to hereinafter as HEMA) and poly(ethylene glycol) methacrylate (referred to hereinafter as PEG-MA). It is expected that a wide range of polar vinyl monomers would be capable of imparting the same effects as HEMA and PEG-MA to polylactide resins and would be effective monomers for grafting. The grafted PLA may contain from about 1 to 20 weight percent of grafted polar monomers, oligomers, or polymers. Preferably, the grafted PLA contains from about 2.5 to 20 weight percent of grafted polar monomers, oligomers, or polymers, and most preferably 2.5 to 10 weight percent of grafted polar monomers, oligomers, or polymers.

Both the HEMA (Aldrich Catalog number 12,863-8) and the PEG-MA (Aldrich Catalog number 40,954-5) used in the Examples are supplied by Aldrich Chemical Company. The PEG-MA purchased from Aldrich Chemical Company is poly(ethylene glycol) ethyl ether methacrylate having a number average molecular weight of approximately 246 grams per mol.

The method for making the grafted polylactide compositions has been demonstrated by a reactive-extrusion process. The grafting reaction can also be performed in other reaction devices as long as the necessary mixing of PLA with HEMA and/or PEG-MA, and any other reactive ingredients, is achieved and enough energy is provided to effect the grafting reactions.

Other reactive ingredients which may be added to the compositions of this invention include, but are not limited to, initiators such as LUPERSOL®101 (referred to hereinafter as L101), a liquid, organic peroxide available from Elf Atochem North America, Inc. of Philadelphia, PA. Free radical initiators useful in the practice of this invention include, but are not limited to, acyl peroxides such as benzoyl peroxide; dialkyl, diaryl, or aralkyl peroxides, such as di-t-butyl peroxide; dicumyl peroxide; cumyl butyl

peroxide; 1,1 di-t-butyl peroxy-3,5,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; 2,5-dimethyl-2,5-bis (t-butylperoxy) hexyne-3 and bis(a-t-butyl peroxyisopropylbenzene); peroxyesters such as t-butyl peroxyisovalate; t-butyl peroctoate; t-butyl perbenzoate; 2,5-dimethylhexyl-2,5-di(perbenzoate) t-butyl di(perphthalate);
5 dialkyl peroxymonocarbonates and peroxydicarbonates; hydroperoxides such as t-butyl hydroperoxide, p-methane hydroperoxide, pinane hydroperoxide and cumene hydroperoxide; and ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide. Azo compounds such as azobisisobutyronitrile may also be used.

Furthermore, other components known in the art may be added to the graft
10 polymers of the present invention to further enhance the properties of the final material. For example, polyethylene glycol may be further added to improve melt viscosity. Other additives may also be incorporated to provide specific properties as desired. For example, anti-static agents, pigments, colorants, and the like may be incorporated into the polymer composition. Additionally, processing characteristics may be improved by
15 incorporating lubricants or slip agents into blends made from polymers of the present invention. All of these additives are generally used in relatively small amounts, usually less than 3 weight percent of the final composition.

The mixture of the polylactide and the polar monomer, oligomer, or polymer is subjected to mechanical deformation in a suitable mixing device, such as a Bradender
20 Plasticorder, a roll mill, a single or multiple screw extruder, or any other mechanical mixing device which can be used to mix, compound, process or fabricate polymers. A particularly desirable reaction device is an extruder having one or more ports. In a preferred embodiment, the reaction device is a co-rotating, twin-screw extruder, such as a ZSK-30 twin-screw compounding extruder manufactured by Werner & Pfleiderer
25 Corporation of Ramsey, New Jersey. This extruder allows multiple feeding and venting ports.

The presence of PLA or modified PLA in blends used to make fibers, films and other shaped articles reduces the water sensitivity of pure PVOH in use. PLA grafted
30 with a polar monomer or a mixture of monomers is preferred for enhanced compatibility with PVOH in order to obtain superior processing and mechanical and physical properties. It is possible to use the blends to make shapes other than fibers or films and to thermally form the blends into complex shapes.

As used herein, the term "water-dispersible" means that the composition dissolves or breaks into pieces smaller than 20 mesh after being immersed in water for
35 approximately five minutes. The term "water-disintegratable" means that the composition breaks into multiple pieces within five minutes of immersion in water and that some of the pieces will be caught by a 20 mesh screen without slipping through in the same manner as

a thread through the eye of a needle. The term "water-weakenable" means that the composition remains in one piece but weakens and loses rigidity after five minutes of immersion in water and becomes drapeable, i.e. it bends without an external force applied thereto, when it is held by one side at a horizontal position. The term "water-stable" means that the composition does not become drapeable after five minutes of immersion in water and remains in one piece after the water response test.

As used herein, the term "graft copolymer" means a copolymer produced by the combination of two or more chains of constitutionally or configurationally different features, one of which serves as a backbone main chain, and at least one of which is bonded at some point(s) along the backbone and constitutes a side chain. The molar amount of the grafted monomer, oligomer or polymer, i.e. side-chain species, may vary but desirably should be greater than the molar amount of the parent species. The term "grafted" means a copolymer has been created which comprises side chains or species bonded at some point(s) along the backbone of a parent polymer. The term "blend" as applied to polymers means an intimate combination of two or more polymer chains of constitutionally or configurationally different features which are not bonded to each other. Such blends may be homogenous or heterogeneous. Preferably, the blend is a homogeneous blend.. (See Sperling, L.H., Introduction to Physical Polymer Science 1986 pp. 44-47 which is herein incorporated by reference in its entirety.) Preferably, the blend is created by combining two or more polymers at a temperature above the melting point of each polymer.

The present invention is illustrated in greater detail by the following specific Examples. It is to be understood that these Examples are illustrative embodiments and that the present invention is not to be limited by any of the Examples or details in the description. Rather, the claims appended hereto are to be construed broadly within the scope and spirit of the invention.

EXAMPLES

Example 1 - Reactive-Extrusion of Polylactide with HEMA

A co-rotating, twin-screw extruder, ZSK-30 manufactured by Werner & Pfleiderer Corporation of Ramsey, New Jersey, was used to manufacture the modified PLA of the Examples. The diameter of the extruder was 30 mm. The length of the screws was 1388 mm. This extruder had 14 barrels, numbered consecutively 1 to 14 from the feed hopper to the die. The first barrel, barrel #1, received the PLA and was not heated, but cooled by water. The vinyl monomer, HEMA, was injected into barrel #5 and the LUPERSOL® 101 peroxide by Atochem was injected into barrel #6. Both the monomer and the peroxide were injected via a pressurized nozzle injector. A vacuum port for devolatilization was included at barrel #11. The die used to extrude the modified PLA strands had four openings of 3 mm in diameter which were separated by 7 mm. The modified PLA strands were then cooled in a cold water bath and then pelletized.

The PLA was fed into the extruder with a volumetric feeder at a throughput of 20 lb/hr. The HEMA and the peroxide were injected into the extruder at throughputs of 1.8 lb/hr and 0.09 lb/hr, respectively. The screw speed was 300 rpm.

The following extruder barrel set temperatures were used during the extrusion run:

<u>Zone 1</u>	<u>Zone 2</u>	<u>Zone 3</u>	<u>Zone 4</u>	<u>Zone 5</u>	<u>Zone 6</u>	<u>Zone 7</u>
180°C	180°C	180°C	180°C	180°C	170°C	160°C

The vacuum was turned on for devolatilization at barrel #11 and the process was allowed to stabilize. The extruded HEMA grafted PLA (PLA-g-HEMA) strands were cooled in a cold water bath and then pelletized.

Melt rheology tests were performed on the modified and unmodified PLA on a Goettfert Rheograph 2000 available from Goettfert in Rock Hill, SC. The modified PLA of this Example was prepared with 9 weight percent HEMA and 0.45 weight percent LUPERSOL® initiator. The weight percentages of the HEMA and LUPERSOL® initiator were based on the weight of the PLA.

The melt rheology tests were performed at 180°C with a 30/1 (length/diameter) mm/mm die. The apparent melt viscosity was determined at apparent shear rates of 50, 100, 200, 500, 1000, and 2000 1/s. A rheology curve was plotted for each material of the apparent viscosity versus the apparent shear rates below.

Sample	Extruded Control PLA supplied by Aldrich	Grafted PLA PLA-g-HEMA (9%, 0.45%)
Apparent Shear Rate (1/s)	Apparent Shear Viscosity (Pa*s)	Apparent Shear Viscosity (Pa*s)
49.997	325.7	97.71
99.994	252.42	97.71
199.99	207.63	65.14
499.97	154.71	55.369
1000	112.35	46.407
2000	82.235	38.675

The apparent melt viscosities at the various apparent shear rates were plotted and rheology curves for the unmodified PLA and the modified PLA of the above Example were generated as shown in Figure 2. The rheology curve of the modified PLA demonstrates the unexpected, reduced viscosities of the modified PLA when compared to the unmodified PLA. These reduced viscosities of the modified PLA result in improved processability of the PLA. The grafting of polar monomers, oligomers or polymers onto PLA results in improved compatibility with both polar materials and polar substrates.

10 Example 2 - Fibers Made From Blends Comprising PVOH and Modified PLA or Unmodified PLA

The water-responsive fibers of the following Example are comprised of a melt blend of polyvinyl alcohol (PVOH) and either unmodified PLA or PLA as modified in Example 1. The range of the compositions for water-responsive fibers varies from about 1 to about 99 weight percent of unmodified or modified PLA in the blend. The modified PLA used in the blends is as described above in Example 1 and the unmodified PLA used in the blends was that as supplied by Aldrich Chemical Company. The PVOH used in the blends was Ecomaty AX10000 supplied by Nippon Gohsei, Japan and is a cold-water soluble polymer synthesized from partially hydrolyzed polyvinyl acetate and containing side chain branches. The melt flow rate of the PVOH used was 100 g/10 min. at 230°C and 2.16 kg.

Extrusion Process for Polymer Blending

Water-responsive blend compositions were prepared by a melt extrusion process. It is preferred to blend or mix the two components in an extruder such as a twin-screw or even a single-screw extruder under appropriate temperature and shear/pressure conditions. The blending process can also be performed in a batchwise mixing device, such as a melt mixer or a kneader, which is discussed in the next section. Both PVOH and unmodified or modified PLA can be fed to an extruder either simultaneously or in

sequence to minimize any adverse effects on the polymers such as degradation or discoloration.

5 In this Example, the extrusion process of the blends was performed using a Haake TW-100, a counter-rotating, twin-screw extruder. The extrusion set temperatures for the four heating zones were 170, 180, 180 and 168°C. The screw speed was 150 rpm. A resin mixture of PLA or modified PLA and PVOH was fed into the extruder at a rate of 10 lb/hr. The melt was extruded, air-cooled and then pelletized.

10 Extruded blend compositions which contained 20, 30, and 40 weight percent of either PLA or modified PLA of Example 1 and 80, 70, and 60 weight percent PVOH, respectively, were produced and used for fiber-spinning.

Melt Mixing Process for Polymer Blending

15 Water-responsive blend compositions were also prepared by a melt mixing process. In this Example, the melt mixing process was performed using a Haake RHEOMIX® 600, a counter-rotating, twin roller mixer. The mixer set temperature was 180°C. The screw speed was 150 rpm. Seventy grams of total resin mixture was fed into the mixer and blended for five minutes. The melt was removed from the mixer and then cooled in air.

20 Melt mixer compositions, which contained 50 and 60 weight percent of either PLA or modified PLA of Example 1 and 50 and 40 weight percent of PVOH, were produced and used for fiber-spinning.

Fiber Processing of the Blends

25 The fibers were made on small-scale fiber spinning processing equipment. The device consists of a vertically mounted cylinder heated by cartridge heaters. A vertically mounted Worm Gear Jactuator (Model: PKN-1801-3-1, manufactured by Duff-Northon Company, Charlotte, North Carolina) was used to extrude the materials into fibers.

30 The fibers were spun from a spin plate with 3 openings of 0.356 mm. The fibers exiting the die were wound on a drum having both reciprocating and rotary movements to collect fiber samples.

Fibers were prepared with varying amounts of PVOH and the unmodified PLA or modified PLA of Example 1.

Example A) PLA/PVOH 20/80 weight ratio fibers.

35 The temperature of the cylinder was set at 360°C. At this temperature, soft fibers were made from this polymer blend which was comprised of unmodified polylactide and polymer vinyl alcohol. The fibers were slightly yellowish.

Example B) PLA-g-HEMA/PVOH 20/80 weight ratio fibers.

This sample was made from the HEMA grafted PLA and polyvinyl alcohol. The temperature of the barrel was also set at 360°C. This polymer blend was made into fibers of less color than the fibers made from the unmodified blend above. These fibers were nearly colorless. This polymer blend exhibited substantially higher melt strength than the blend containing unmodified PLA, presumably due to the improved compatibility of the HEMA grafted PLA with PVOH. As a result, fibers and films can be extruded at higher extrusion rates than from the blends containing unmodified PLA. Fibers can be produced in a temperature range from 353 to 371°C.

10 Example C) PLA/PVOH 30/70 weight ratio fibers.

This blend composition was also spun into fibers. Some melt fracture occurred.

Example D) PLA-g-HEMA/PVOH 30/70 weight ratio fibers.

Soft and nearly colorless fibers were made from this blend composition. This blend showed improved processability over the unmodified PLA/PVOH 30/70 blend.

Example E) PLA/PVOH 40/60 weight ratio fibers.**Example F) PLA-g-HEMA/PVOH 40/60 weight ratio fibers.****Example G) PLA/PVOH 50/50 weight ratio, mixer blended fibers.****Example H) PLA-g-HEMA/PVOH 50/50 weight ratio, mixer blended fibers.****20 Example I) PLA/PVOH 60/40 weight ratio, mixer blended fibers.****Example J) PLA-g-HEMA/PVOH 60/40 weight ratio, mixer blended fibers.**

The blends containing HEMA grafted PLA had lower viscosities than the blends containing unmodified PLA and thus could be extruded at higher rates and exhibited improved processability. Additionally, the fibers from the blends containing modified PLA exhibited less discoloration than fibers from the blends containing unmodified PLA, suggesting improved compatibility of the modified PLA. All of the blends containing HEMA grafted PLA exhibited higher melt strength and better fiber processability than those containing unmodified PLA blends at the same weight ratios.

30 Water Response Test of the HEMA grafted PLA/PVOH Fibers

For each of the above compositions, a section of the prepared fiber was cut measuring about one inch long. The diameter of the fiber was measured and recorded. The water-response test involved using a pair of tweezers to hold the section of the fiber, immersing it into a scintillation vial filled with 20 milliliters of water and holding it there for five minutes. After five minutes, the cap was placed on the scintillation vial and the vial was placed in a Model 75 Shaker (available from Burrell Corp., Pittsburgh, PA). The vial was shaken for 30 seconds with the shaker set at maximum speed. If the fiber

- began to disperse or disintegrate, the contents of the scintillation vial were emptied through a 20 mesh screen (20 mesh U.S.A. Standard Testing Sieve, ASTM E-11 Specification, No. 20). The vial was then rinsed with 20 milliliters of water from a squeeze bottle to remove any remaining fiber pieces and emptied through the sieve. If the
- 5 fiber did not disperse or disintegrate, the fiber was observed for any loss in rigidity.

Water-Responsiveness Map
for Extruder and Mixer Blended Fiber Compositions

10	Weight Percent of unmodified or modified PLA in Blends with PVOH		
	1 <-----> 40	50	60 <-----> 99
	Dispersible	Weakenable	Stable

- 15 Fibers made from blend compositions were water-dispersible up to about 40 weight percent of modified or unmodified PLA in the blend. The fibers made from blends with about 60 or greater weight percent of unmodified or modified PLA were water-stable. The fibers made from blends between these two ranges should be
- 20 considered water-weakenable. The fibers made from blends with about 50 weight percent of unmodified or unmodified PLA were water-weakenable.

Example 3 - Films Made From Blends Comprising PVOH and Modified PLA or Unmodified PLA

- 25 The water-responsive films of the following Examples are composed of melt blends of unmodified or modified PLA and PVOH. The range of the compositions for water-responsive films vary from 1 to 99 weight percent of unmodified or modified PLA in the blend. The presence of PLA or modified PLA in the blend used to make films reduces the water sensitivity of pure PVOH in use. PLA grafted with a polar monomer or
- 30 a mixture of monomers is preferred for enhanced compatibility with PVOH in order to obtain superior mechanical and physical properties. The modified PLA used in the blends is as described above in Example 1 and the unmodified PLA used in the blends was that as supplied by Aldrich Chemical Company. The PVOH used in the blends was Ecomaty AX10000 supplied by Nippon Gohsei, Japan, a cold-water soluble polymer synthesized
- 35 from partially hydrolyzed polyvinyl acetate containing side branches.

Extrusion Process for Polymer Blending

Water-responsive blend compositions were prepared by a melt extrusion process. It is preferred to blend or mix the two components in an extruder such as a twin-screw or even a single screw extruder under appropriate temperature and shear/pressure conditions. The blending process can also be performed in a batchwise mixing device, such as a melt mixer or a kneader, which is discussed in the next section. Both PVOH and modified PLA can be fed to an extruder either simultaneously or in sequence to minimize any adverse effects on the polymers such as degradation or discoloration.

In these Examples, the extrusion process of the blends was performed using a Haake TW-100, a counter-rotating, twin-screw extruder. The extrusion set temperatures for the four heating zones were 170°C, 180°C, 180°C and 168°C. The screw speed was 150 rpm. A resin mixture of PLA or modified PLA and PVOH was fed into the extruder at a rate of 10 lb/hr. The melt was extruded, air-cooled and then pelletized.

Extruded blend compositions, which contained 20, 30, and 40 weight percent of either unmodified PLA or modified PLA and 80, 70 and 60 weight percent PVOH, respectively, were produced and used to make films in this Example.

Melt Mixing Process for Polymer Blending

Water-responsive blend compositions were also prepared by a melt mixing process. In these Examples, the melt mixing process was performed using a Haake RHEOMIX® 600, a counter-rotating, twin roller mixer. The mixer set temperature was 180°C. The screw speed was 150 rpm. 70 grams of total resin mixture was fed into the mixer and blended for five minutes. The melt was removed from the mixer and then cooled in air.

Melt mixer compositions, containing 30, 40, 50 and 60 weight percent HEMA grafted PLA and 70, 60, 50 and 40 weight percent PVOH, respectively, were produced and used to make the films in this Example.

Film Preparation

A film was prepared for each blend composition using a Carver hot press with two heated platens at a temperature of 190°C and a pressure of 15,000 psi for about one minute. The thickness of the films in this Example were approximately 4 mils. However, the thickness of the films could be either increased or decreased depending on the final use and properties desired.

Water Response Test of the HEMA grafted PLA/PVOH Films

For each of the compositions, a section of the prepared film was cut measuring about 1/4 of an inch by about 1/2 of an inch. The water-response test involved using a pair of tweezers to hold the section of the film, immersing it into a scintillation vial filled with 20 milliliters of water and holding it there for five minutes. After five minutes, the cap was placed on the scintillation vial and the vial was placed in a Model 75 Shaker (available from Burrell Corp., Pittsburgh, PA). The vial was shaken for 30 seconds with the shaker set at maximum speed. If the film began to disperse or disintegrate, the contents of the scintillation vial were emptied through a 20 mesh screen (20 mesh U.S.A. Standard Testing Sieve, ASTM E-11 Specification, No. 20). The vial was then rinsed with 20 milliliters of water from a squeeze bottle to remove any remaining film pieces and emptied through the sieve. If the film did not disperse or disintegrate, the film was observed for any loss in rigidity.

Water-Responsiveness Map
for Extruder and Mixer Blended Film Compositions

20	Weight Percent of unmodified or modified PLA in Blends with PVOH		
	1 <-----> 40	50	60 <-----> 99
	Dispersible	Weakenable	Stable

Films made from blend compositions were water-dispersible up to about 40 weight percent of modified or unmodified PLA in the blend. The films made from blends with about 60 or greater weight percent of unmodified or modified PLA were water-stable. The films made from blends between these two ranges should be considered water-weakenable. The films made from blends with about 50 weight percent of unmodified or unmodified PLA were water-weakenable.

It is to be understood that these Examples are illustrative embodiments and that this invention is not to be limited by any of the Examples or details in the description. Rather, the claims appended hereto are to be construed broadly within the scope and spirit of the invention. Particularly, it is to be understood that the invention includes but is not limited to compositions, films, fibers and articles in which the claimed composition, film or fiber is a component in the final product.

Claims

We claim:

- 5 1. A polymer composition comprising a polylactide grafted with a polar monomer, oligomer, polymer or a combination thereof.
2. The polymer composition of Claim 1, wherein said polar monomer is an ethylenically, unsaturated monomer containing at least one polar functional group or said
10 oligomer or said polymer is an oligomer or a polymer polymerized from an ethylenically unsaturated monomer containing at least one polar functional group.
3. The polymer composition of Claim 2, wherein said at least one polar functional group is a hydroxyl, carboxyl or sulfonate group or a combination thereof.
- 15 4. The polymer composition of Claim 3, wherein said at least one polar functional group is a hydroxyl group.
5. The polymer composition of Claim 1, wherein said polar monomer is a polar
20 vinyl monomer.
6. The polymer composition of Claim 1, wherein said polar monomer, oligomer, or polymer is selected from the group consisting of 2-hydroxyethyl methacrylate and polyethylene glycol methacrylate and derivatives thereof.
- 25 7. The polymer composition of Claim 6, wherein said polar monomer, oligomer, or polymer is 2-hydroxyethyl methacrylate or its derivatives.
8. The polymer composition of Claim 1, wherein said polylactide contains from 1
30 to 20 weight percent grafted polar monomer, oligomer or polymer or combination thereof.
9. The polymer composition of Claim 1, wherein said polylactide is melt blended with a second polymer.
- 35 10. The polymer composition of Claim 9, wherein said composition is water-dispersible, water-weakenable or water-stable.

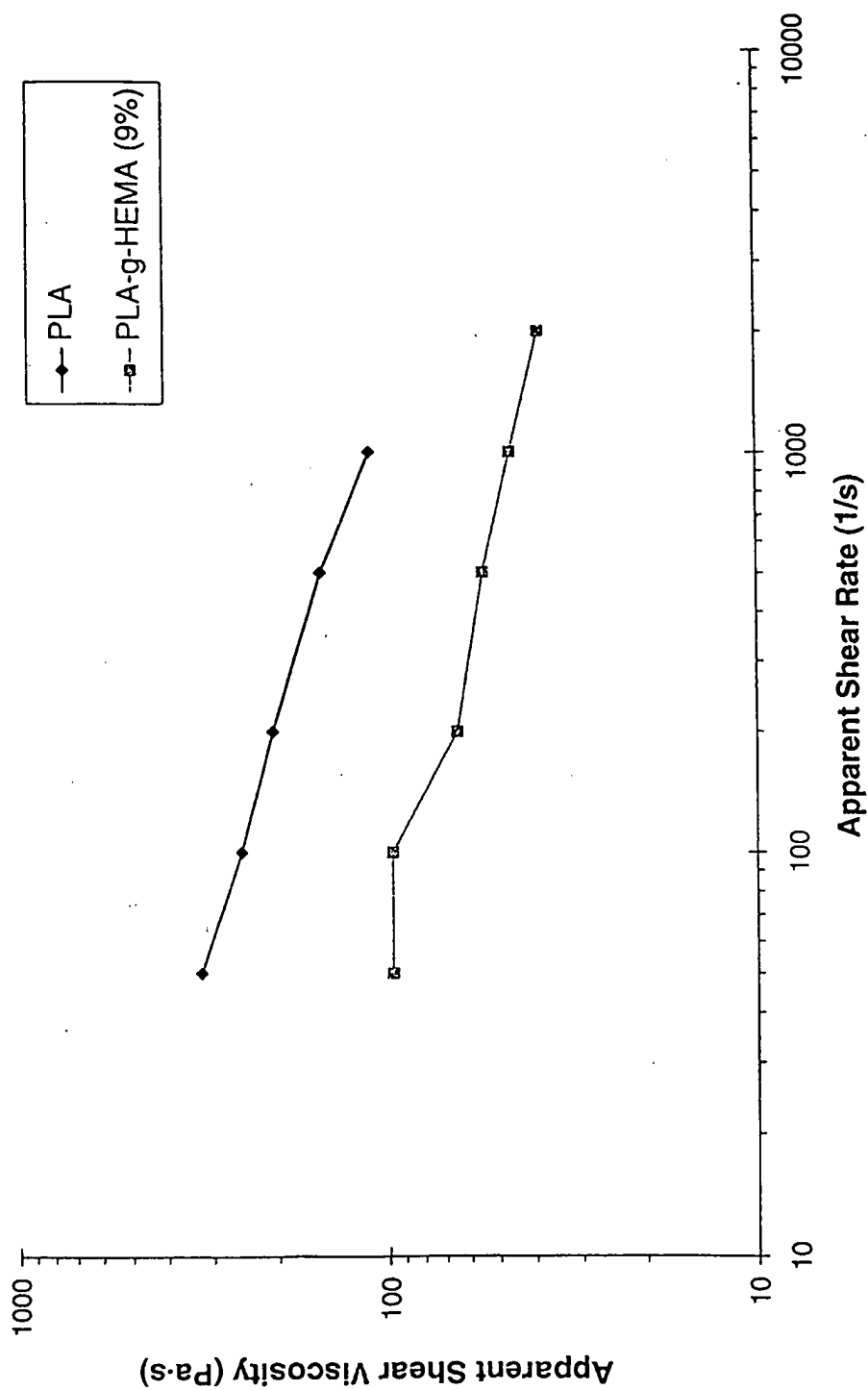
11. A polymer composition comprising a polylactide backbone with a plurality of polar monomers, oligomers, polymers or mixture thereof grafted onto said polylactide backbone.
- 5 12. A method of making a grafted polylactide composition comprising the steps of:
a) combining a polylactide and a polar monomer, oligomer, or polymer in a reaction vessel; and
b) providing sufficient energy to the combination of said polylactide and said polar monomer, oligomer, or polymer in order to form said grafted polylactide
10 composition.
13. The method of Claim 12, wherein said reaction vessel is an extruder.
14. The method of Claim 13, wherein said extruder is a co-rotating, twin-screw
15 extruder.
15. The method of Claim 12, wherein said polar monomer is an ethylenically unsaturated monomer containing at least one polar functional group or said oligomer or said polymer is an oligomer or a polymer polymerized from an ethylenically unsaturated
20 monomer containing at least one polar functional group.
16. The method of claim 15, wherein said at least one polar functional group is a hydroxyl, carboxyl or sulfonate group or a combination thereof.
- 25 17. The method of Claim 12, wherein said polar monomer is a polar vinyl monomer.
18. The method of Claim 12, wherein said polar monomer, oligomer, or polymer is selected from the group consisting of 2-hydroxyethyl methacrylate and polyethylene glycol methacrylate and their derivatives.
30
19. The method of Claim 12, wherein said sufficient energy is provided in the form of heat.
- 35 20. The method of Claim 12, wherein an initiator is added to the mixture.
21. A film or a fiber comprising a blend of a poly(vinyl alcohol) and a polylactide.

22. The film or fiber of Claim 21, wherein said polylactide is modified.
23. The film or fiber of Claim 22, wherein said polylactide is grafted with a polar
5 monomer, oligomer, or polymer or a combination thereof.
24. The film or fiber of Claim 23, wherein said polar monomer is an ethylenically
unsaturated monomer containing at least one polar functional group or said oligomer or
said polymer is an oligomer or a polymer polymerized from an ethylenically unsaturated
10 monomer containing at least one polar functional group.
25. The film or fiber of Claim 24, wherein said at least one polar functional group
is a hydroxyl, carboxyl or sulfonate group or a combination thereof.
- 15 26. The film or fiber of Claim 25, wherein said at least one polar functional group
is a hydroxyl group.
27. The film or fiber of Claim 24, wherein said polar monomer is a vinyl
monomer.
20
28. The film or fiber of Claim 23, wherein said polar monomer, oligomer, or
polymer is selected from the group consisting of 2-hydroxyethyl methacrylate and
polyethylene glycol methacrylate and derivatives thereof.
- 25 29. The film or fiber of Claim 27, wherein said polar monomer, oligomer, or
polymer is selected from the group consisting of 2-hydroxyethyl methacrylate and its
derivatives.
30. The film or fiber of Claim 21, wherein said blend comprises about 1 to about
30 99 weight percent poly(vinyl alcohol) and about 1 to about 99 weight percent polylactide.
31. The film or fiber of Claim 30, wherein said blend comprises about 40 to about
80 weight percent poly(vinyl alcohol) and about 20 to about 60 weight percent
polylactide.
35
32. The film or fiber of Claim 30, wherein said blend comprises about 1 to about
40 weight percent polylactide and is water-dispersible.

33. The film or fiber of Claim 30, wherein said blend comprises about 40 to about 60 weight percent polylactide and is water-weakenable.
- 5 34. A method of making a film or fiber comprising the steps of:
a) blending a poly(vinyl alcohol) with a polylactide; and
b) extruding a film or a fiber from the blend.
- 10 35. The method of Claim 34, wherein said polylactide is modified prior to blending with the poly(vinyl alcohol).
36. The method of Claim 35, wherein said polylactide is modified by the steps comprising:
a) combining a polylactide and a polar monomer, oligomer, or polymer in a
15 reaction vessel; and
b) providing sufficient energy to the combination of said polylactide and said polar monomer, oligomer, or polymer in order to modify said polylactide.
- 20 37. The method of Claim 34, wherein the film or fiber is water-dispersible and comprises about 1 to about 40 weight percent polylactide and about 60 to about 99 weight percent poly(vinyl alcohol).
- 25 38. The method of Claim 34, wherein the film or fiber is water-weakenable and comprises about 40 to about 60 weight percent polylactide and about 40 to about 60 weight percent poly(vinyl alcohol).
- 30 39. The method of Claim 34, wherein the film or fiber is water-stable and comprises about 60 to about 99 weight percent polylactide and about 1 to about 40 weight percent poly(vinyl alcohol).
40. The method of Claim 34, wherein the blending is performed by melt extrusion.

1 / 1

Figure 1. Melt Rheology at 180°C for PLA and HEMA Grafted PLA



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/15968

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F283/02 C08L67/04 C08L51/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 525 671 A (EBATO HIROSHI ET AL) 11 June 1996 see column 10, line 1-7 ---	1,2
X	US 4 745 160 A (CHURCHILL JEFFREY R ET AL) 17 May 1988 see column 6, line 31-46 ---	1
X	US 4 921 934 A (BIXLER KATHLEEN J ET AL) 1 May 1990 see column 5, line 19-21 ---	1
X	US 5 654 381 A (LOTAN NOAH ET AL) 5 August 1997 see claim 1 ---	1
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 October 1998

Date of mailing of the international search report

29/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3018

Authorized officer

Meulemans, R

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 98/15968

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 567 510 A (RUTHERFORD DENISE R ET AL) 22 October 1996 see column 4, line 17-31 see column 8, line 38-44 ----	21,30,31
A	US 5 200 247 A (WU PAI-CHUAN ET AL) 6 April 1993 see claim 1 ----	21
P,X	WO 98 29506 A (KIMBERLY CLARK CO) 9 July 1998 see the whole document -----	21,30, 31,34, 37-40

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15968

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5525671 A	11-06-1996	EP 0661325 A JP 7233245 A	05-07-1995 05-09-1995
US 4745160 A	17-05-1988	AU 587977 B AU 4315085 A CA 1247271 A DK 287885 A EP 0166596 A FI 852374 A, B GR 851474 A IE 58678 B JP 7069929 A JP 7106987 B JP 7069930 A JP 7106988 B JP 2018465 C JP 7051517 B JP 61015846 A NO 175135 B PT 80710 B US 4877606 A	07-09-1989 02-01-1986 20-12-1988 27-12-1985 02-01-1986 27-12-1985 25-11-1985 03-11-1993 14-03-1995 15-11-1995 14-03-1995 15-11-1995 19-02-1996 05-06-1995 23-01-1986 30-05-1994 20-10-1987 31-10-1989
US 4921934 A	01-05-1990	AU 2752188 A EP 0321913 A JP 1213323 A MX 14264 A PT 89284 A, B	29-06-1989 28-06-1989 28-08-1989 01-12-1993 29-12-1989
US 5654381 A	05-08-1997	NONE	
US 5567510 A	22-10-1996	US 5472518 A AU 693978 B AU 4240496 A CA 2206921 A CN 1171825 A EP 0800595 A WO 9621057 A US 5630972 A US 5508101 A US 5763065 A	05-12-1995 09-07-1998 24-07-1996 11-07-1996 28-01-1998 15-10-1997 11-07-1996 20-05-1997 16-04-1996 09-06-1998

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15968

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5200247 A	06-04-1993	NONE	
WO 9829506 A	09-07-1998	AU 5522798 A	31-07-1998

THIS PAGE BLANK (USPTO)